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Electrical switching and memory phenomena in *o*-tolidine DDQ under pressure

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Abstract. Electrical switching has been observed in *o*-tolidine-DDQ at pressures of 7·66 GPa and fields $\sim 3 \times 10^5$ *V/m* with $\sigma_{ON}/\sigma_{OFF} \approx 10^3$ at a temperature of 300 K. The switching is found to be of the memory type and the sample can be driven back to the low conducting state by applying ac pulses of sufficient magnitude but independent of frequency.

Keywords. High pressure; non-ohmic conduction; electrical switching.

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1. Introduction

Many of the charge transfer complexes show non-ohmic conduction and electrical switching under pressure (Subramanyam and Hemamalini Naik 1986). Effect of pressure on electrical switching in semiconducting glasses was studied by Johnson and Quinn (1978). Other systems which show electrical switching are insulating films of mylar, anthracene thin films (Elsharkawi and Kao 1977), Cu-TCNQ (Potember *et al* 1979), $NbSe_3$ (Zettl and Gruner 1982) and in the mixed-stack charge transfer crystal tetrathiafulvalene-*p*-chloranil (Yoshinori Tokura *et al* 1988).

Current-voltage characteristics of *o*-tolidine-DDQ were studied up to a pressure of 7·66 GPa. Low field behaviour is ohmic and transition to a square law region is observed at a field of approximately 10^5 *V/m* before the sample switches. At a pressure of 7·66 GPa and a field of 3×10^5 *V/m*, the sample switches from low conducting OFF state of several kiloohms to high conducting ON state of several ohms with $\sigma_{ON}/\sigma_{OFF} \approx 10^3$. AC pulses of sufficient magnitude drive the sample from ON state to OFF state.

2. Experimental

The charge transfer complex *o*-tolidine-2,3-dichloro-5,6-dicyano-*p*-benzoquinone (*o*-tolidine-DDQ) was prepared by the procedure due to Brass and Clar (1956) using benzene as solvent medium in the stoichiometric ratio 1:1. The starting materials were purified by repeated crystallization. *o*-tolidine-DDQ grown was an amorphous material.

High pressure studies were done in Bridgman anvil cell described by Bandyopadhyay *et al* (1980a, b). Electrical contacts were made by pressure using high purity copper

leads. Compacted pellets (typical dimensions 1 mm × 0·25 mm × 0·25 mm) were used for electrical measurements. I–V measurements were done by two-probe method. The current up to 30 mA was driven by a constant current source constructed in our laboratory and voltage up to 250 V was measured using a Keithley 193A system DMM at the same points of contact to the sample.

3. Results

Pressure dependence of resistivity is shown in figure 1. Resistance falls exponentially with pressure. At 7·66 GPa resistance falls by two orders of magnitude from that at atmospheric pressure. Above a pressure of nearly 4 GPa, resistance begins to drift slowly upwards with time at constant pressure. Drift is larger at higher pressures. In figure 1 bars above the circled data points show resistance at the end of five minutes at constant pressure. Rate of drift decreases with time. As pressure increases due to the increased overlap of the molecular orbitals the resistance of the sample decreases.

Sample of *o*-tolidine-DDQ shows switching behaviour at a pressure of 7·66 GPa at room temperature. At lower pressures, up to the maximum applied voltage it does not exhibit switching property but increased non-linearity with pressure is observed.

Figure 2 shows I–V characteristics at different pressures. At low fields, behaviour is ohmic and above a critical field, transition to square law region is observed before switching at a pressure of 7·66 GPa. Switching field is $\sim 3 \times 10^5$ *V/m*. At switching field, the sample switches from OFF state of low conductivity to ON state of high conductivity with $\sigma_{ON}/\sigma_{OFF} \sim 10^3$. Near the switching region, voltage is unstable and at certain pressures, with constant driving current, voltage steadily increases to maximum voltage.

After the sample switches to high conducting ON state, as current increases a differential negative resistance region with unstable voltage is observed. As current

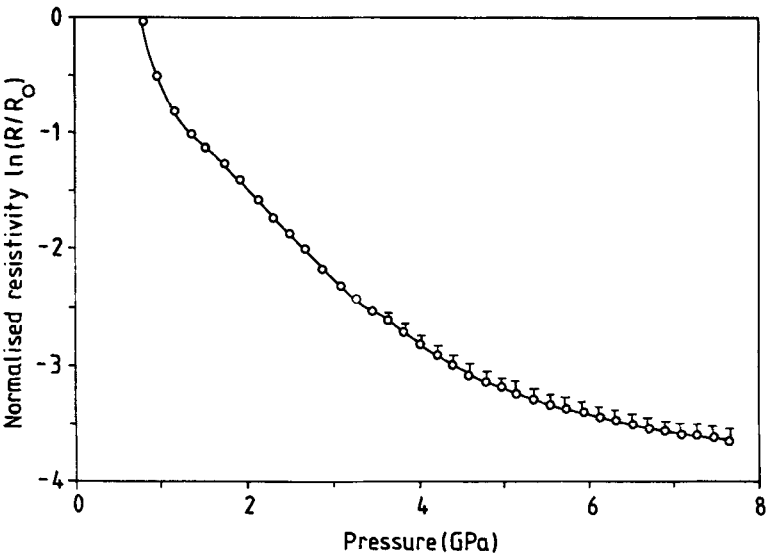

Figure 1. Pressure dependence of normalized resistivity of *o*-tolidine-DDQ, $T = 300$ K.

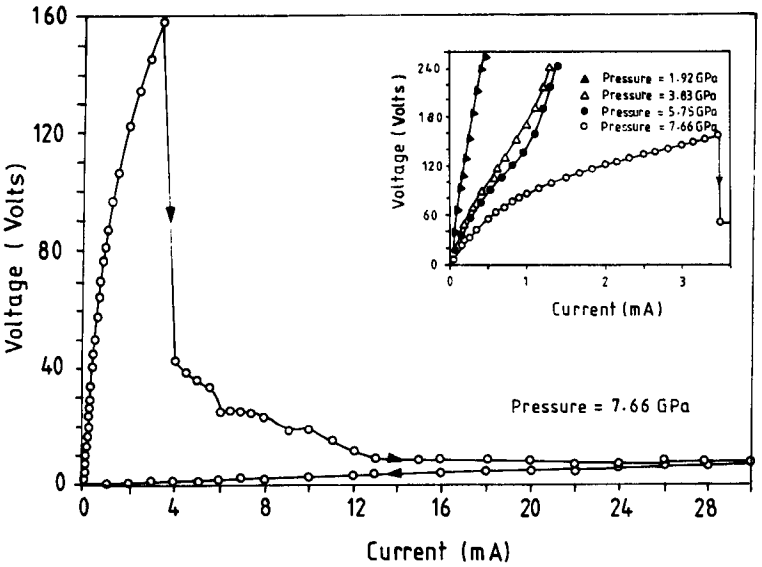

Figure 2. Current-voltage characteristics of *o*-tolidine-DDQ at different pressures, temperature = 300 K.

is reversed instability in voltage vanishes as shown in figure 2. I–V characteristics show hysteresis which becomes lesser as we repeat the experiment. On removing the bias, sample remains in the ON state for a short period. On subsequent I–V measurements, after removing the bias, sample remains in the ON state for a time of the order of seconds. This time becomes larger as we repeat the experiment a number of times. AC pulses of amplitude nearly 5 V drives the system to OFF state (Hemamalini Naik and Subramanyam 1986). This does not seem to depend on the frequency. The amplitude of the sinusoidal signal needed to switch the sample to OFF state increases as we repeat the experiment. On repeated cycling, degradation in phenomenon is observed.

4. Discussion

Functional form of resistivity *vs.* pressure is exponential with a fall of resistance of two orders of magnitude at a pressure of 7·66 GPa from ambient pressure.

Ln–Ln plot of current-voltage relation at a pressure of 7·66 GPa is shown in figure 3. At low fields slope is found to be unity and at higher fields $\sim 1 \times 10^5$ *V/m* a transition to square law region is observed. In the non-linear region current is due to space charge limited current (Gutman and Lyons 1967; Farges *et al* 1972). For space charge limited current to occur, applied voltage V has to be greater than a critical voltage. In this case injected free carrier concentration dominates at equilibrium over thermally generated carrier concentration. For a trap free solid, current density $J = x\mu V^2/t^3$, where x is the dielectric constant of the medium, μ is the mobility and t is the electrode spacing.

Before the sample switches, ln I *vs.* $V^{1/2}$ is a straight line above a field $\sim 7 \times 10^4$ *V/m*. This non-ohmic region can arise either from electrode limited Schottky emission or

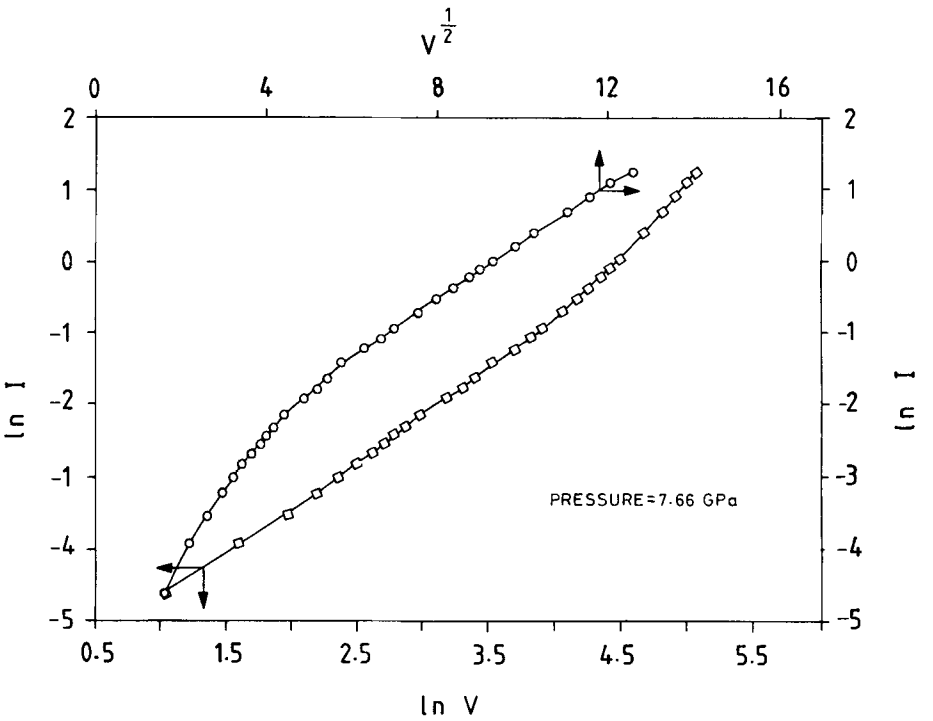

Figure 3. Plot of ln I *vs.* ln V and ln$I$ *vs.* $V^{1/2}$ of *o*-tolidine-DDQ at a pressure of 7·66 GPa.

from bulk Poole-Frenkel effect (figure 3). Detailed study of dielectric behaviour at high frequencies is needed to confirm this. Current I due to Poole-Frenkel effect (Adkins *et al* 1970) is

$$I = I_0 \exp \frac{e(\beta V^{1/2} - V_g)}{k_B T} \text{ with } \beta = \left(\frac{e}{\pi \varepsilon \varepsilon_0 t}\right)^{1/2}$$

where I_0 is a constant, V_g is the energy difference between the trap level and bottom of the conduction band, ε_0 is the permittivity of free space, ε is the relative dielectric permittivity, T is the absolute temperate, k_B is the Boltzmann constant and e is the charge of the electron. In the Poole-Frenkel effect, field induced thermal ionization from discrete traps to conduction band enhance the conduction electron density. The model of hydrogenic impurities in which the diameter of electron's ground state orbit is several interatomic spacing can manifest the Poole-Frenkel effect. Switching observed in this sample can be a field induced phase transition similar to that of *o*-tolidine-iodine (Hemamalini Naik and Subramanyam 1986).

5. Conclusion

Non-ohmic conduction of the charge transfer complex *o*-tolidine-DDQ increases with applied pressure and finally the sample switches at a field $\sim 3 \times 10^5$ *V/m*, at a pressure of 7·66 GPa and temperature of 300 K. Non-ohmic conduction can arise from either

space charge limited current or Poole-Frenkel effect. The switching is of the memory type and can be erased by ac pulses of sufficient magnitude.

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